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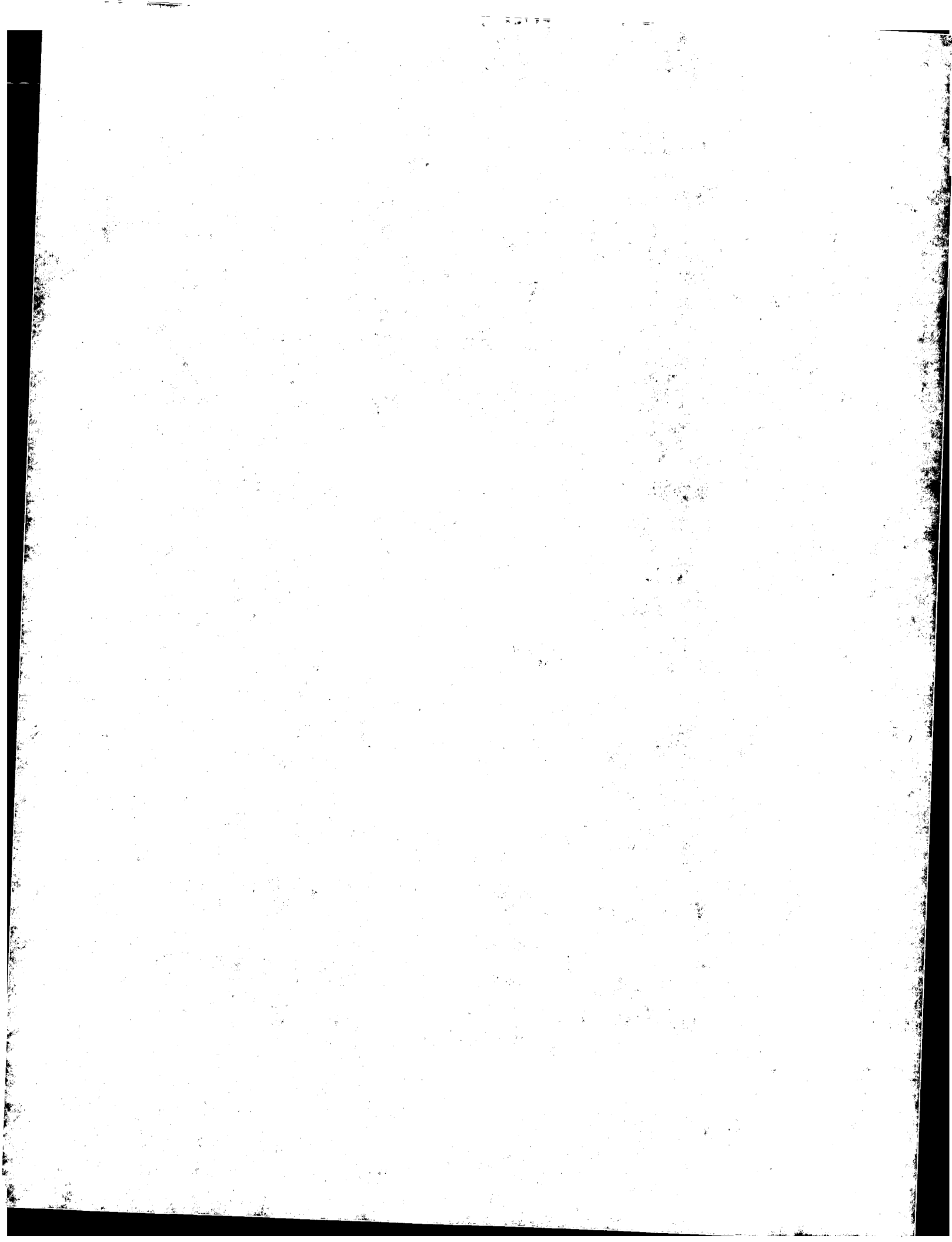
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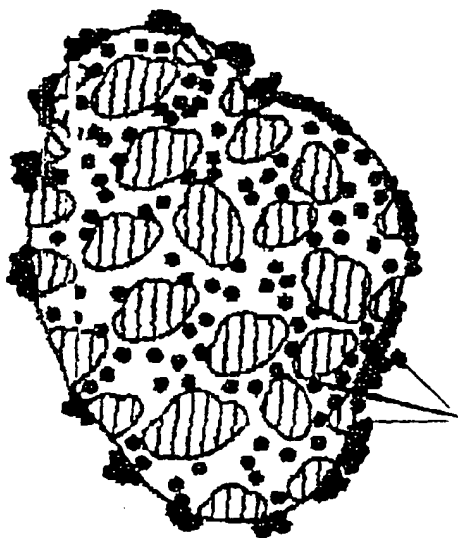
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(54) Title: ADSORBENT MATERIALS FOR TREATING BIODEGRADABLE WASTE AND PROCESS FOR THEIR PREPARATION



Hydrophobic  
silica  
nano-particles

(57) Abstract: The present invention provides a specifically designed highly porous particle, having a size of >1 micron passively and/or actively filled with nano-size particles to form a new coated or stuffed particle having desired properties in managing and treating biodegradable waste. Said porous particle may optionally contain additional material(s) such as photocatalysts, bacteria, pesticides, herbicides, spores of algae, seeds of water-plants, eggs of snails and/or worms.

Schematic view of porous particle  
(perlite) stuffed with nano-particles  
(hydrophobic silica)

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ADSORBENT MATERIALS FOR TREATING BIODEGRADABLE WASTE AND PROCESS FOR THEIR  
PREPARATION

### **Field of the Invention**

This invention relates to the field of waste management and particularly to materials specifically designed for application as materials associated with controlling malodor manure and the application of such materials in the treatment of biodegradable waste.

### **Background of the Invention**

Animal waster including excreta, food remains, and animal bedding typically accumulate in a husbandry of commercial animal production. Such accumulated substances need to be properly managed. Animal manure, particularly its odor and excessive nutrient concentrations, are a serious and a growing problem, especially in the field of commercial animal husbandry. There is a global need for the development and improvement of waste management and odor control facilities and method associated with animal husbandry, e.g. in the beef cattle industry, dairy industry, poultry industry and in swine industry.

Manure can be handled as a liquid, a semi-solid or a solid. The amount of bedding and dilution water influences manure characteristics. These characteristics affect the type of manure management system suitable for waste treatment. Typically, solid manure is a combination of bedding and feces. Semi-solid manure is a combination of feces, urine and some bedding

and no extra liquid is added, while liquid manure has water added to form a floatable mixture.

Many factors have to be considered when choosing the type of manure management system for a specific animal production operation. These include: the livestock type (cattle, hogs, poultry), the age and size of animal, the feed required, the housing system, the bedding required or available, the cropping practice of the area, proximity to waterways, proximity to neighboring residential areas and the personal preference of the livestock grower.

One of the most common and basic manure treatment facility is the lagoon system, which may be used regardless of the animal managed in the operation. Lagoons originated as a means of storing and conserving fertilizer nutrients from the waste of animals up until the time it was applied directly to the soil.

Lagoons act as digesters in which two major types of bacteria decompose organic matter into liquids and sludge: anaerobic bacteria, typically present in the intestinal tract of warm blooded animals and are active under oxygen-free conditions; and aerobic bacteria which are active only in the presence of dissolved oxygen, resulting either from diffusion across the water surface of the lagoon, or as a result of photosynthesis by algae. Lagoon systems, however, yield a loss of nutrient value. Further, as malodors are prevalent in most lagoon systems, frequent sludge removal is required, especially if the lagoon is undersized for the operation and there is a need for water level

control and mechanical aeration systems to keep the lagoon in operation. Such removal may increase the cost of the operation.

The malodors released from the manure present a major environmental problem. Odor in livestock operations is the direct result of the decay of organic materials, be it feces or feed products and the resulting high concentrations of ammonia, hydrogen sulfide, carbon dioxide, trace gases, volatile organic compounds, methane dust and some pathogens.

The odor may be treated by ventilation, either by natural wind-propelled ventilation, by mechanical ventilation using fans, ventilation, tunnels, etc. Alternatively, the released odor may be reduced by the use of biofilters or biomass filters, or by covering the storage structures (e.g., lagoon) with either high density polyethylene materials or straw, corn stalks, etc., the latter having the limitation that they become soaked with water and thus sink, thereby contributing to manure solid and odor problems in the storage tank.

US patent 3,884,804 deals with a method of treating animal wastes to reduce odors produced by the decomposition of the organic materials in the animal wastes. The following systems were discussed:

1. Contacegon particles, comprising solid catalyst particles having surface portions which are wetproofed by treatment with a hydrophobic material, are floated on the surface of a watery mass containing the animal wastes. The Contacogen particles promote the oxidation by air of the odoriferous compounds produced by the degenerative breakdown of the animal wastes.

The Contacogen particles are solid catalyst particles which have been treated with a hydrophobic agents selected from the group consisting of polytetrafluoroethylene, silicon resins and silica colloids made hydrophobic by surface conversion to silicone. The catalyst particles may be any substance presenting a large specific surface area which has the property of catalyzing the oxidation by air of the odoriferous compounds produced by the degenerative breakdown of animal wastes. Activation carbon is such a catalyst.

2. Floating on the surface of a watery mass of animal wastes solid catalyst particles selected from the group consisting of carbon and activated carbon particles having surface portions of a hydrophobic material which forms a discontinuous film thereon. The hydrophobic materials are selected from the group described above. The size of carbon particles may vary from about 10 micron (for a powder) to relatively large size granules (about 1 cm).

We have found that hydrophobic particles of a smaller size than 10 microns are highly effective in treatment of liquid and semi-solid animal manure. More specifically, floatable hydrophobic and/or hydrophilic particles having a diameter of less than 1 $\mu$ m in association with floatable, high porous particles, having both hydrophilic and hydrophobic groups play an important role in a highly effective management of animal waste. In our pending Israeli Applications 133,364 and 137,735, we have described a process for treatment of animal manure comprising formation



of a distinct surface layer (referred to as an "interface layer") over the upper face of the animal waste pool. Same interface layer has multiple functions, based on its chemical composition and physical structure, and provides changes in the properties and composition of the upper pool layers. The interface layer may contain different components, in accordance with the desired function to be achieved. Said components comprising:

(a) Floatable, substantially hydrophobic nanoparticles having a diameter of less than 100 nm, and preferably, 2-40nm. Such particles may be, for example, modified silica (for example, alkyl-silica), modified minerals (such as, alkyl-mineral materials), and others.

(b) Floatable, high porous (over 50% of the material consisting of pores) particles having both hydrophobic and hydrophilic groups. Such materials may be for example, silica minerals, alumina minerals, clay minerals, plant-material residues (wood pieces, wood pulp, sawdust, straw, etc.). Same particles, having a diameter of  $>1\mu\text{m}$ , may optionally be associated with (1) said substantially hydrophobic nanoparticles; with or without (2) substantially hydrophilic nanoparticles, having a diameter of less than 100 nm, and preferably, 2-40nm. Such particles may be, for example, silica, alumina, and other oxygen-containing minerals; and/or (3) photocatalysts capable of decomposing organic material and malodors; and/or (4) aerobic bacteria capable of degrading organic waste materials.

(c) Active carbon particles in association with component (a) and/or component (b).

More specifically, the nanoparticle represents a nano-size, non-porous, mechanically rigid and highly dispersable particle whereas the highly porous particle represents a porous, micron-to-cm size, mechanically brittle particle. Furthermore, a nano-size particle has a huge outer convex surface per volume or weight, whereas the highly porous particle has a huge inner concave surface due to the pores and holes.

In spite of the above differentiation between the particles, both particles may be consisted of the same or different materials and they may be subjected to the same or different pre-treatment procedures for rendering hydrophobic and/or hydrophilic properties.

According to the present invention, we have found that a  $>1$  micron, highly porous, particle may be specifically designed to play an effective role in managing and treating animal waste pool. More specifically, the porous particle may be filled with variable amounts of nano-range particles to form a wide range of coated porous particles starting from partially coated (encapsulated) particle and ending with extensively coated (stuffed) particle. It was further evident that porous particles having different extent of coating play different roles in managing and treating of animal waste pools.

It is an object of present invention to provide a novel highly porous particle which represents a particular combination of  $>1$  micron porous particle and nanoparticles, for obtaining a specifically designed particle highly effective in managing and treating animal waste pools. The animal waste includes feces, typically also urine, and at times, also animals bedding material and food remains. It is a further object of present invention to provide a specifically designed highly porous particle, having a size of  $>1$  micron, passively and or actively filled with nano-size particles to form a new particle having desired properties in managing and treating animal waste in a receptacle suitable for collecting such waste. The receptacle may be a receptacle which directly receives the animal waste preferably positioned underneath the animal growing facility. Alternatively, the receptacle may be an "open" or "closed" flow-less (rest) reservoir situated outside the animal growing facility to which the animal waste is transferred through pipes or channels, by the use gravity caused flow or various pumping arrangements, etc. the receptacle containing the animal waste will be referred to herein as the "animal waste pool".

It is yet an another object of present invention to use the same specifically designed highly porous particle, containing the nano-size particles for preventing, reducing and/or removing malodors typically associated with such animal wastes.

### Summary of the Invention

The present invention provides a specifically designed highly porous particle, having a size of  $>1$  micron passively and/or actively filled with nano-size particles to form a new coated or stuffed particle having desired properties in managing and treating biodegradable waste. Said porous particle may optionally contain additional material(s) such as photocatalysts, bacteria, pesticides, herbicides spores of algae, seeds of water-plants, eggs of snails and/or worms.

### Description of Figures

Fig. 1A-B: A schematic illustration of a porous perlite spheroid particle adsorbing on its external surface and on its pores surface hydrophobic silica nanno particles.

A: A porous perlite spheroid particle "stuffed" with silica nanoparticles.

B: A porous perlite spheroid particle "encapsulated" with nanoparticles.

Fig. 2A-C: Schematic illustrations of a variety of adsorption options of nanoparticles onto the surface of a perlite particle.

A. Concave surfaces of the perlite particle (for example on the pore inner surface) adsorb the nanoparticles.

B. Convex surfaces of the perlite particle (for example on the outer surface) adsorb the nanoparticles.

C. Concave and convex surfaces of the perlite partice adsorb nanoparticles.

Fig. 3a-e: Schematic illustrations of optional methods for encapsulation and/or stuffing of macro-particles with nanoparticles.

- a. A schematic illustration of an optional method (nanoparticles are flowing through the macro-particles) for stuffing macro-particles with nanoparticles.
- b. A schematic illustration of an optional method (using vacuum and a container for storing nanoparticles and liquid, when present) for encapsulation and/or stuffing of macro-particles with nanoparticles.
- c. A schematic illustration of an optional method (using vacuum and nanoparticles and liquid stored in separate containers) for encapsulation and/or stuffing of macro-particles with nanoparticles.
- d. A schematic illustration of an optional method (using vacuum and a container for storing nanoparticles and solid chemical reagents, when present) for encapsulation and/or stuffing of macro-particles with nanoparticles.
- e. A summary of optional procedures for encapsulation and/or stuffing of macro-particles with nanoparticles.

### Detailed Description of the Invention

A specifically designed combination of >1 micron highly porous particle and nanoparticles has been established for providing a particular particle having a unique structure that is highly effective in managing and treating a wide range of animal waste pool types.

Such combination comprising floatable, high porous (over 80% of the material consisting of pores) >1 micron particles having both hydrophobic and hydrophilic groups (hereinafter referred to as "particle B"). Such materials may be for example, silica minerals (for example, perlite), alumina minerals, clay minerals (for example, claydite), plant-material residues (wood pieces, wood pulp, sawdust, straw, etc.). Same porous particle filled either on its surface and/or within its pores with (1) substantially hydrophobic nano-range particles having a diameter of less than 100 nm, and preferably, 1-40nm (hereinafter referred to as "particle A"). Such hydrophobic nano-range particles may be, for example, modified silica (for example, alkyl-silica), modified minerals (such as, alkyl-mineral materials), and others, and/or (2) substantially hydrophilic nano-range particles (hereinafter referred to as "particle C") having a diameter of less than 100 nm, and preferably, 1-40nm. Such nano-range hydrophilic particles may be, for example, silica, alumina, and other oxygen-containing minerals. The particles A and C have a huge outer convex surface per volume or weight, whereas the particle B has an outer convex surface and a huge inner concave surface due to the internal pores and holes. Thus, a combination of particles A (and/or C) with particles B in which the nanoparticles are stuffed within the pores of the particles B provides having huge areas of The particles A and C have a huge outer convex surface per volume or weight, whereas the particle B has an outer convex surface and a huge inner concave surface due to the internal pores and holes. Thus, a combination of

particles A (and/or C) with particles B in which the nanoparticles are stuffed within the pores of the particles B provides particles B both convex and concave shapes, including various labyrinths. Fig. 1 demonstrates a schematic illustration of a porous perlite spheroid particle adsorbing on its external surface and on its pores surface hydrophobic silica nanno particles. Fig. 1A represents a porous perlite spheroid particle actively “stuffed” with nanoparticles. Fig. B represents a porous perlite spheroid particle passively “encapsulated” with nanoparticles.

Due to the presence of both, concave surfaces (for example, the pores’ inner surface) and convex surfaces (for example, the particle’s outer surface) there are many optional adsorption alternatives resulted in multiple of surface-particle and particle-particle interactions. Fig. 2 depicts the principal adsorption options of nanoparticles onto the adjacent surfaces of the porous particle. Fig. 2A represents a state in which the two adjacent surfaces (a and b) are concave and the adsorbed nanoparticles are either hydrophobic, hydrophilic or mixture thereof. Fig. 2B represents a state in which the two adjacent surfaces (a and b) are convex and the adsorbed nanoparticles are either hydrophobic, hydrophilic or mixture thereof. Fig. 2C represents a state in which one of the adjacent surfaces (a) is convex and the other (b) is concave and the adsorbed nanoparticles are either hydrophobic, hydrophilic or mixture thereof. It can be seen that the proximity of the nanoparticles adsorbed on the (a) and (b) surfaces is dependent on the concave-convex configuration of the adjacent surfaces.

The extent of combination between the nanoparticles and particles B, from just passive encapsulation (Fig. 1B) to actively and extensively stuffing (Fig. 1A), specifically determines the role of the designed structure of the particle B in the managing and treating the waste pool. For example, stuffed particles B are less permeable to light and to low mass components and consequently the more of the heavy mass components are accumulated and concentrated in the vicinity of the liquid layer boundary. Thus, the extent of "stuffing" of particles B with nanoparticles (particles A and/or C) determines the permeability of the interface layer and consequently, have a major role on both, the selectivity and time dependent permeability of the interface layer. On the contrary, the less stuffed particles B may form a more permeable interface layer that allows migration of the heavier mass components to the surface.

The specifically designed particles B coated with particles A (and/or C) determine the method of treatment and managing of different animal waste pools and the products obtained from such treatments.

The specifically designed structure consists of two ways of coating of particles A (and/or C) onto particles B: In the first way the particles A (and/or C) are "passively" coated mainly on the outer surface of the particles B. In such case, there is no movement of nanoparticles through the pores of the porous particle. Passive encapsulation is achieved for example, by mixing the dry porous particles with the powdery



nanoparticles. In the second way, the particles A (and/or B) are "actively" coating (stuffing) the particles B, namely, simultaneously filling the numerous pores and coating the outer surface of the particles B. This can be done by moving the nanoparticles through the porous particles. In other words, the porous particle serves as a filter for the nanoparticles passing through.

Basically, there are several options for designing a specific structure of particle B coated with either particles A (and/or C), with or without additional components. For example:

1. Stuffing particles B by particles A (and/or C) using means for flowing the nanoparticles through the particles B. In this method, the nanoparticles are contained within separate bellow(s) and they are pushed into a container containing particles B. (Fig. 3a).
2. Coating (encapsulating and/or stuffing) particles B by particles A (and/or C) using vacuum pump. In this method, the nanoparticles are contained in a separate container and they are pushed (using a vacuum pump) into a container containing particles B in which they are mixed together (Fig. 3b). The same device is applicable for stuffing the nanoparticles into the pores of the particles B by means of a liquid, in which the nanoparticles are immersed.
3. Encapsulating and/or stuffing particles B by particles A (and/or C) using vacuum pump. In this method, the nanoparticles are contained in a separate container and they are pushed (using a vacuum pump) into a

container containing particles B. A liquid is contained in another container to provide a stream of droplets that are mixed with the nanoparticles before their arrival to the container of the particles B (Fig. 3c). The same device is applicable for coating nanoparticles with various solid or liquid chemical reagents before they are transferred to the container of the particles B.

4. Coating (encapsulating and/or stuffing) particles B by pre-coated particles A (and/or C) using vacuum pump. In this method, the nanoparticles are contained in a separate container with various solid or liquid chemical reagents before they are pumped into the container of the particles B (Fig. 3).

A scheme of the various encapsulating and stuffing procedures are summarized in Fig. 3e.

In summary, there should be a wide scope of method and devices applicable for preparing any desired combination, according to the present invention, between nanoparticles and >1 micron particles to form specifically designed structures highly effective in managing and treating of animal waste pools.

The specifically designed structure which is basically consisted of a particular combination of particles A (and/or C) and a particle B, may be optionally provided with further components and materials according to the type of waste pool under treatment. Such additional components may

be in a solid or a liquid form, for example, the liquids  $\text{TiCl}_4$ ,  $\text{AlCl}_3$  or  $\text{SiCl}_4$  which release an acid upon getting in contact with water; glycerin or glycerin-like material which avoids the formation of too-dusty product; poly-siloxane which forms a degradable film over the surface of the designed particles B; non-toxic photocatalytic metal (or complex thereof) selected from the group of Al, Fe, Cu, Ti, Co or Ni (such as, for example,  $\text{TiO}_2$  and  $\text{Al}_2\text{O}_3$ ); conductive particles, such as graphite and metals which create electrical contact between hydrophobic and hydrophilic centers of said particles B and A (and/or C) to increase their catalytic activity and rate of oxidation/reduction reactions. Other added materials may be, for example, spores of algae, seeds of water-plants, eggs of snails and/or worms, pesticidal and/or herbicidal materials, and any other component that may play a role in managing and treating the animal waste pools.

It should be noted that in spite of the above differentiation between particles A (or C) and B, either of the particles may be of the same or different materials and they may be subjected to the same or different pre-treatment procedures for rendering hydrophobic and/or hydrophilic properties.

### Examples

#### Particles A (and/or C) + B + algae spores and/or seed of water- plants

This product consists of a specifically designed combination of particles B coated with particles A (and/or C) and it may further contain algae spores and/or seed of water-plants. This product is intended for treating a flow-less "open" (having light) waste pool by means of production of "interface layer" which layer provides a plant-based protein nutritionally foodstuff for feeding animals following removal of the interface layer off the pool.

The process for preparing the mixture contains the step of encapsulation of the particles B with particles A (and/or C), in a weight ratio of at least 95-99% B and 1-5% A and/or C, followed by the addition of 0.1 to 3% (by weight) of the algae spores or the seeds.

#### (b) Particles A (and/or C) + B + eggs of snails and/or worms

This product consists of a specifically designed combination of particles B coated with particles A (and/or C) and it may further contain eggs of snails and/or worms. This product is intended for treating a flow-less "closed" (no light is needed) waste pool by means of production of "interface layer" which layer provides a non-plant rich protein-based nutritionally foodstuff for feeding animals following removal of the interface layer off the pool.

The process for preparing the mixture contains the step of encapsulation of the particles B with particles A (and/or C), in a weight ratio of at least

95-99% B and 1-5% A and/or C, followed by the addition of 0.05 to 2% (by weight) of the eggs.

It should be pointed out that a mixture containing particles A (and/or C)+ B+ eggs of snails and/or worms+algae spores and/or seed of water-plants, is applicable for treating a flow-less "open" (light is needed) waste pool by means of production of "interface layer" which layer provides a high rich protein-based nutritionally foodstuff for feeding animals following removal of the interface layer off the pool.

In such a case, the process for preparing the mixture contains the step of encapsulation of the particles B with particles A (and/or C), in a weight ratio of at least 95-99% B and 1-5% A and/or C, followed by the addition of 0.05 to 2% (by weight) of the eggs and 0.1 to 3% (by weight) of the spores and seeds.

(c) Particles A (and/or C) + B + pesticide and/or herbicide

This product consists of a specifically designed combination of particles B coated with particles A (and/or C) and it may further contain pesticidal and/or herbicidal materials. This product is intended for treating a flow-less "closed" (no light is needed) and "open" waste pools by means of production of "interface layer" which layer is applicable as a fertilizer for various crops following removal of the interface layer off the pool.

The process for preparing the mixture contains the step of encapsulation of the particles B with particles A (and/or C), in a weight ratio of at least

95-99% B and 1-5% A and/or C, followed by the addition of 0.001 to 5% (by weight) of the pesticide and/or herbicide.

(d) Particles A (and/or C) + B + Glycerin solution

This product consists of a specifically designed combination of particles B coated with particles A (and/or C) following immersion of the combined particles within a glycerin solution. This dust-free product is intended for treating a flow-less "closed" and "open" waste pools by means of production of "interface layer".

It should be emphasized that any of the above described products (a) to (c) may be immersed in a glycerin solution to yield a dust-free product.

(e) Particles B + nano-size carbonated particles

This product consists of a specifically designed combination of particles B coated with active nano-size carbonated particles. This product is intended for treating a flow-less "closed" and "open" waste pools by means of production of "interface layer".

The carbonated nano-size particles may be:

- A mixture of natural graphite mill with either particles A and/or C.
- A mixture of soot with either particles A and/or C.
- A mixture of natural graphite and soot.

The connection of carbon to the nanoparticles and/or particles B is by physical adsorption.

The composition contains about 98-99% (by weight) particles B and 1-2% (by weight) of carbonated particles A and/or C. When particle B consists of microsilica particles, the composition contains 90-98% (by weight) microsilica and 2-10% (by weight) carbonated particles A and/or C.

(f) Particles A (and/or C) + B consisting of carbon clustered particles

This product consists of a specifically designed combination of carbon clustered particles B coated with particles A and/or C. This product is intended for treating a flow-less "closed" and "open" waste pools by means of production of "interface layer".

(g) Particles B + C and/or A (wherein particles A and/or C are stuffed into the pores of particles B).

This product consists of a specifically designed combination of particles B actively stuffed with particles A and/or C. This product is intended for treating a flow-less "closed" and "open" waste pools by means of production of "interface layer".

The stuffed particles B are optionally coated by carbon particles.

(h) Particles B + liquid(s) impregnated particles A (and/or C) + polysiloxane

This product consists of a specifically designed combination of particles B coated with liquid-impregnated nano-size particles, followed by treatment

with poly-siloxane (slow mixing or rolling the particles B on the layer of low viscous poly-siloxane, 25-200  $\mu$ , at room temperature) to provide designed particles B coated with a poly-siloxane film. The liquid may be for example,  $TiCl_4$  which, in the presence of water, converts to the photocatalytic  $TiO_2$ .

The process for preparing the mixture contains the step of adding liquid-impregnated particles A (and/or C) to particles B, in a weight ratio of at least 95-99% B and 1-5% A (and/or C). The amount of liquid may range from 0.5 – 95% (by weight) of total product.

This product is intended for treating a flow-less "closed" and "open" waste pools by means of production of "interface layer".

(i) Components B + A (and/or C) + conductive particles

This product consists of a specifically designed combination of particles B passively or actively mixed with particles A and/or C in the presence of conductive material(s), either in a solid or a liquid form, such as, for example, graphite, free metal, a metallic compound, and/or ionic groups.

This product is intended for treating a flow-less "closed" and "open" waste pools by means of production of "interface layer".



### Claims

1. A specifically designed highly porous particle, having a size of >1micron, passively and/or actively filled with nano-size particles to form a new coated or stuffed particle having desired properties in managing and treating biodegradable waste.
2. A new designed particle as claimed in claim 1, wherein the nano-size particles are in the range of 1-40 nanometer.
3. A new designed particle as claimed in claim 1, wherein a liquid is used for filling the said porous particle with nanoparticles.
4. A new designed particle as claimed in claim 3, wherein said liquid releases an acid upon contact with water.
5. A new designed particle as claimed in claim 4, wherein the liquid is a suspension of  $\text{TiCl}_4$ ,  $\text{AlCl}_4$  or  $\text{SiCl}_4$ .
6. A new designed particle as claimed in claims 1 and 3-5, wherein said nanoparticles form a suspension with same liquid before actively or passively filled the highly porous particle.

7. A new specifically designed highly porous particle, according to claim 1, wherein the nano-size particles are substantially hydrophobic (referred to as particles A).
8. A new specifically designed highly porous particle, according to claim 1, wherein the nano-size particles are substantially hydrophilic (referred to as particles C).
9. A new specifically designed highly porous particle, according to any one of the claims 1, 7 and 8, wherein the nano-size particles are a mixture of particles A and C.
10. A composition for managing and treating a waste pool containing the specifically designed highly porous particle, according to claim 1, and at least additional component selected from the group comprising spores of algae, seeds of water-plants, eggs of snails and/or worms.
11. A composition for managing and treating a waste pool containing the specifically designed highly porous particle, according to claim 1, and at least additional component selected from the group comprising pesticidal and/or herbicidal materials.

12. A new specifically designed highly porous particle, according to any one of the preceding claims, wherein said designed particle is treated with an aqueous solution of glycerin or glycerin-like material, before use.

13. A new specifically designed highly porous particle, according to claim 1, wherein said nanoparticles are carbon coated.

14. A new specifically designed highly porous particle, according to claim 1, wherein said designed porous particle is carbon coated.

15. A new specifically designed highly porous particle, according to claim 1, wherein said designed porous particle is coated by a film made of polysiloxane.

16. A new specifically designed highly porous particle, according to claim 1, wherein said particle having at least 80% porosity.

17. A new specifically designed highly porous particle, according to claim 1, wherein said particle containing both hydrophobic and hydrophilic groups.

18. A new specifically designed highly porous particle, according to claim 1, wherein said porous particle and nano-size particles are selected from

the group of compounds named "oxide" and/or oxide group(s) – containing compounds.

19. A new specifically designed highly porous particle, according to claims 1 and 18, wherein said group of compounds named "oxide" and/or oxide group(s) – containing compounds, are selected from the group comprising minerals and mineral-derived particles.

20. A new specifically designed highly porous particle, according to claim 19, wherein said mineral particles are selected from the group comprising silica minerals, alumina minerals and clay minerals.

21. A new specifically designed highly porous particle, according to claim 20, wherein said silica mineral is perlite and said clay mineral is bentonite or claydite.

22. A new specifically designed highly porous particle, according to claims 1 and 18, wherein said porous particle is selected from the group comprising perlite, bentonite and claydite.

23. A new specifically designed highly porous particle, according to claims 1 and 18, wherein said porous particle is selected from the group comprising plant material residues containing amorphous oxide.

24. A new specifically designed highly porous particle, according to claim 23, wherein said plant residue is selected from the group comprising husk straw, peat, dry stems and sawdust.

25. A new specifically designed highly porous particle, according to claims 1 and 7, wherein said substantially hydrophobic nanoparticle (particle A) is alkylated-silica.

26. A new specifically designed highly porous particle, according to claim 1, wherein at least part of said nanoparticles having photo-catalytic activity.

27. A new specifically designed highly porous particle, according to claim 26, wherein said nanoparticles being a heavy metal complex or an oxide of a metal.

28. A new specifically designed highly porous particle, according to claim 27, wherein said heavy metal complex comprises a non-poisonous metal selected from Al, Fe, Cu, Ti, Co or Ni.

29. A new specifically designed highly porous particle, according to claim 26, wherein said nanoparticles having photo-catalytic activity are titanium metal and/or titanium oxide (TiO<sub>2</sub>).

30. A new specifically designed highly porous particle, according to claim 26, wherein said nanoparticle having photo-catalytic activity is  $\text{Al}_2\text{O}_3$ .

31. A new specifically designed highly porous particle, according to claims 1 and 8, wherein said substantially hydrophilic nanoparticle (particle C) is selected from the group comprising  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  or  $\text{TiO}_2$ .

32. A specifically designed highly porous particle, according to claim 1, wherein said designed particle having a size of  $1\mu\text{m}$  to  $5\text{ cm}$ .

33. A specifically designed highly porous particle, according to claim 1, wherein the weight ratio of the porous particle to nanoparticles is 1-5% to 95-99%.

34. A specifically designed highly porous particle, according to claim 1, substantially as described in the specification.

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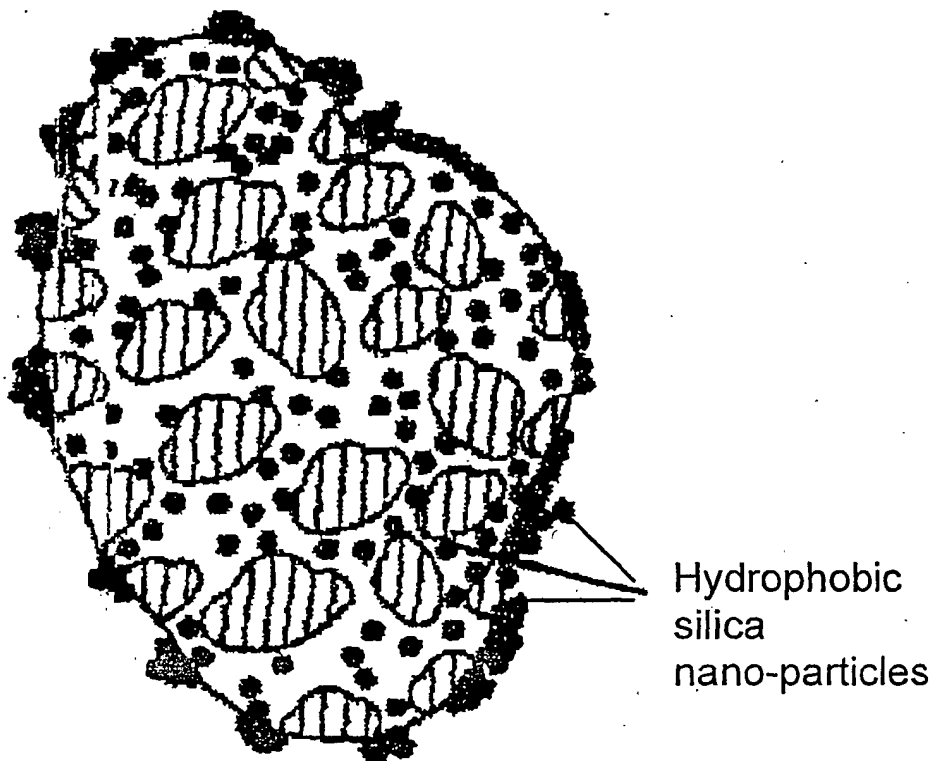


Fig. 1A

Schematic view of porous particle  
(perlite) stuffed with nano-particles  
(hydrophobic silica)

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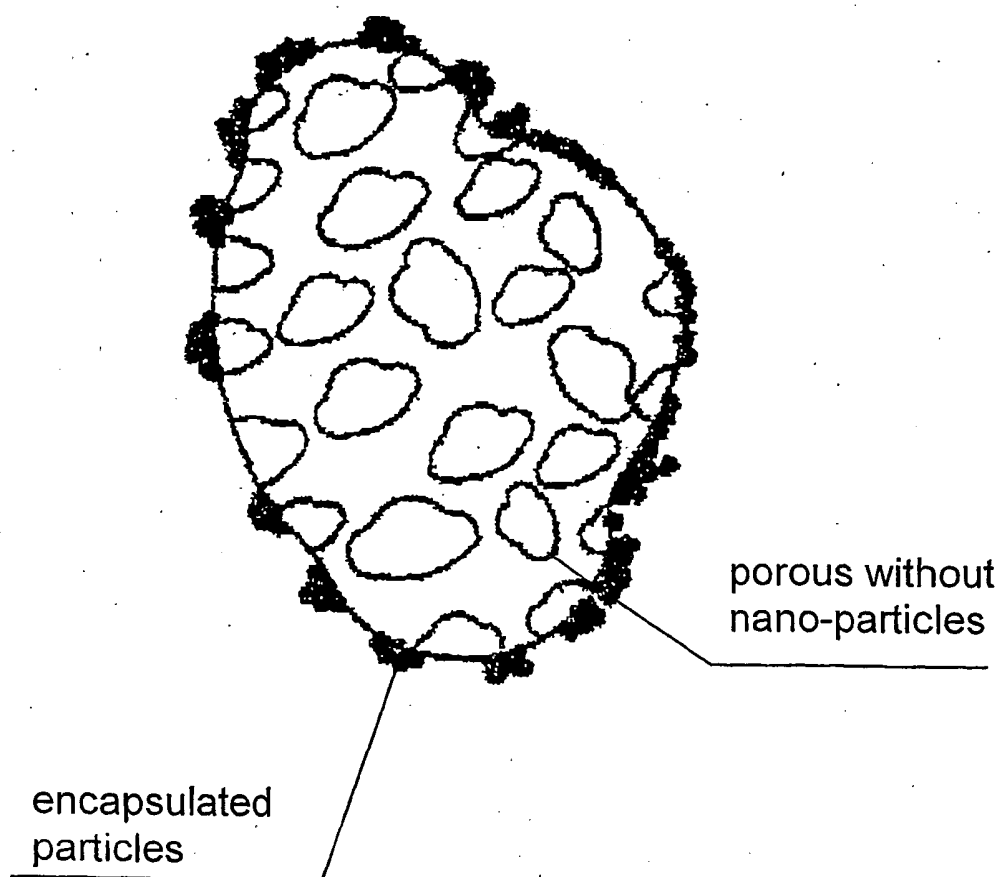
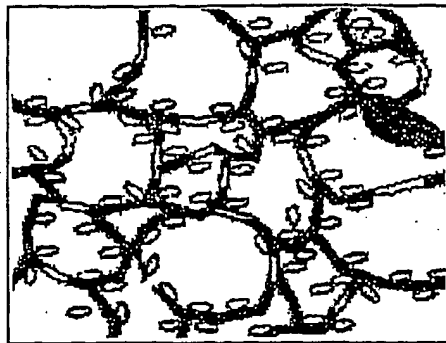


Fig. 1B

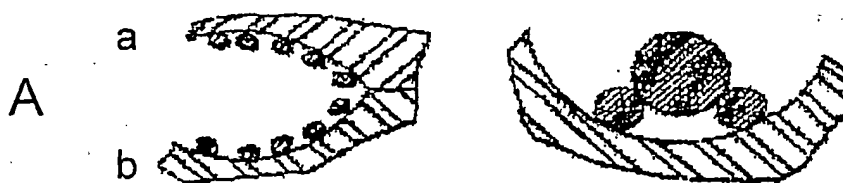
Schematic view of porous particle  
encapsulated with nano-particles  
(hydrophobic silica)



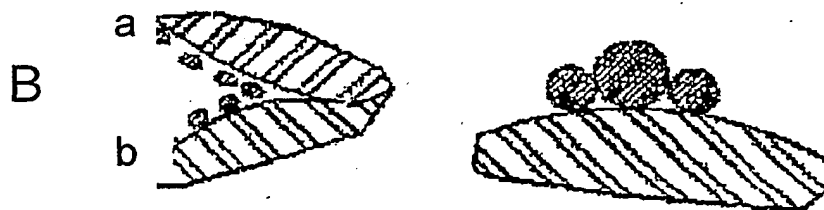
3/8



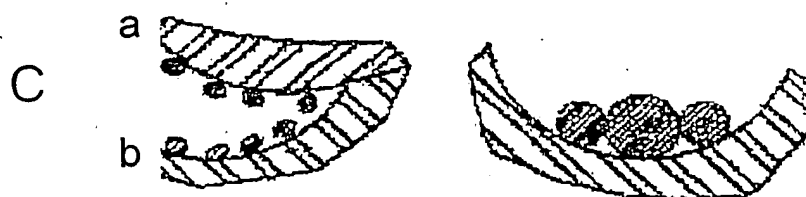
## 1. Concave - Concave



## 2. Convex - Convex



## 3. Concave - Convex



perlite



nanoparticle

Fig. 2

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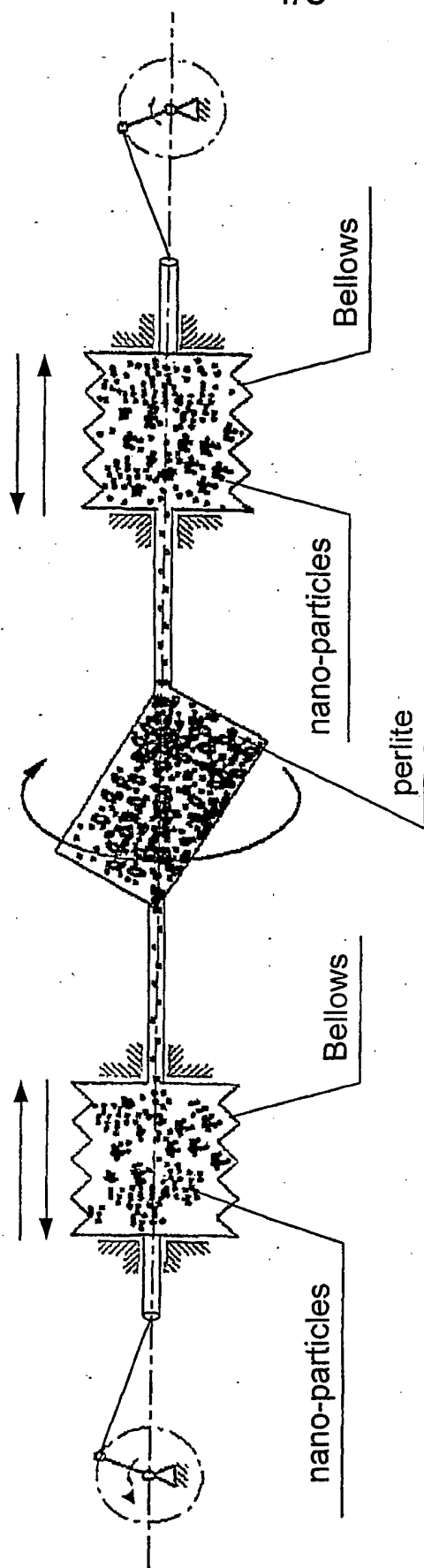


Fig. 3a. Scheme of stuffing nano-particles  
into macro-particles

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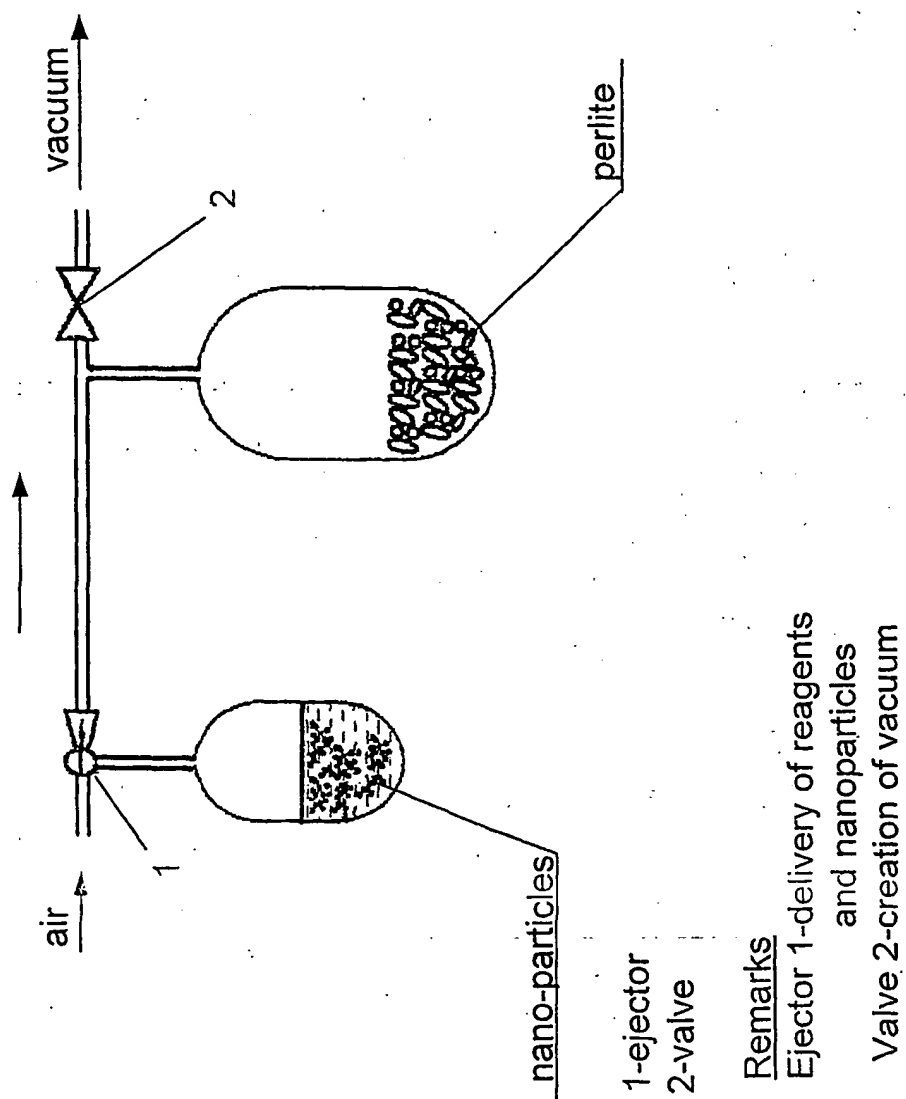
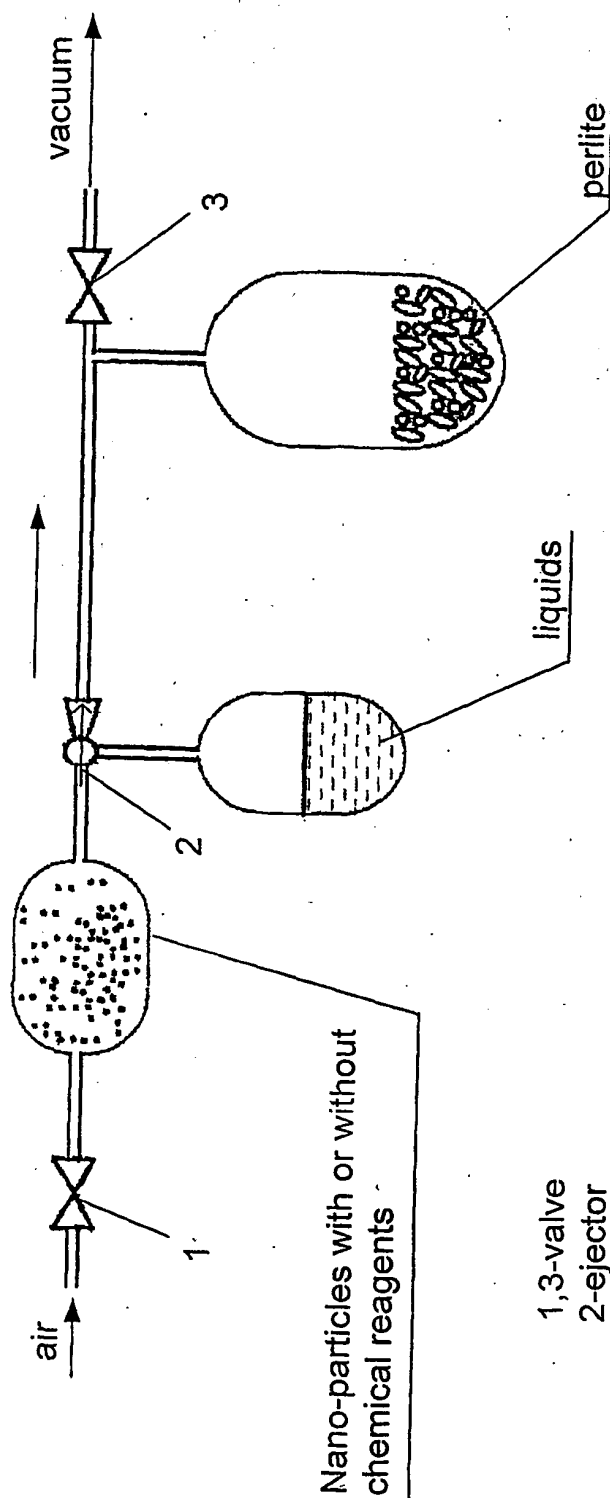


Fig. 3b. Scheme of stuffing of macro-particles  
with nano-particles

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1,3-valve  
2-ejector

#### Remarks

Valve 1-delivery of air  
Valve 3-creation of vacuum  
Ejector 2-delivery of reagents and nanoparticles

Fig. 3C. Scheme of encapsulation and/or stuffing of macro-particles with nano-particles

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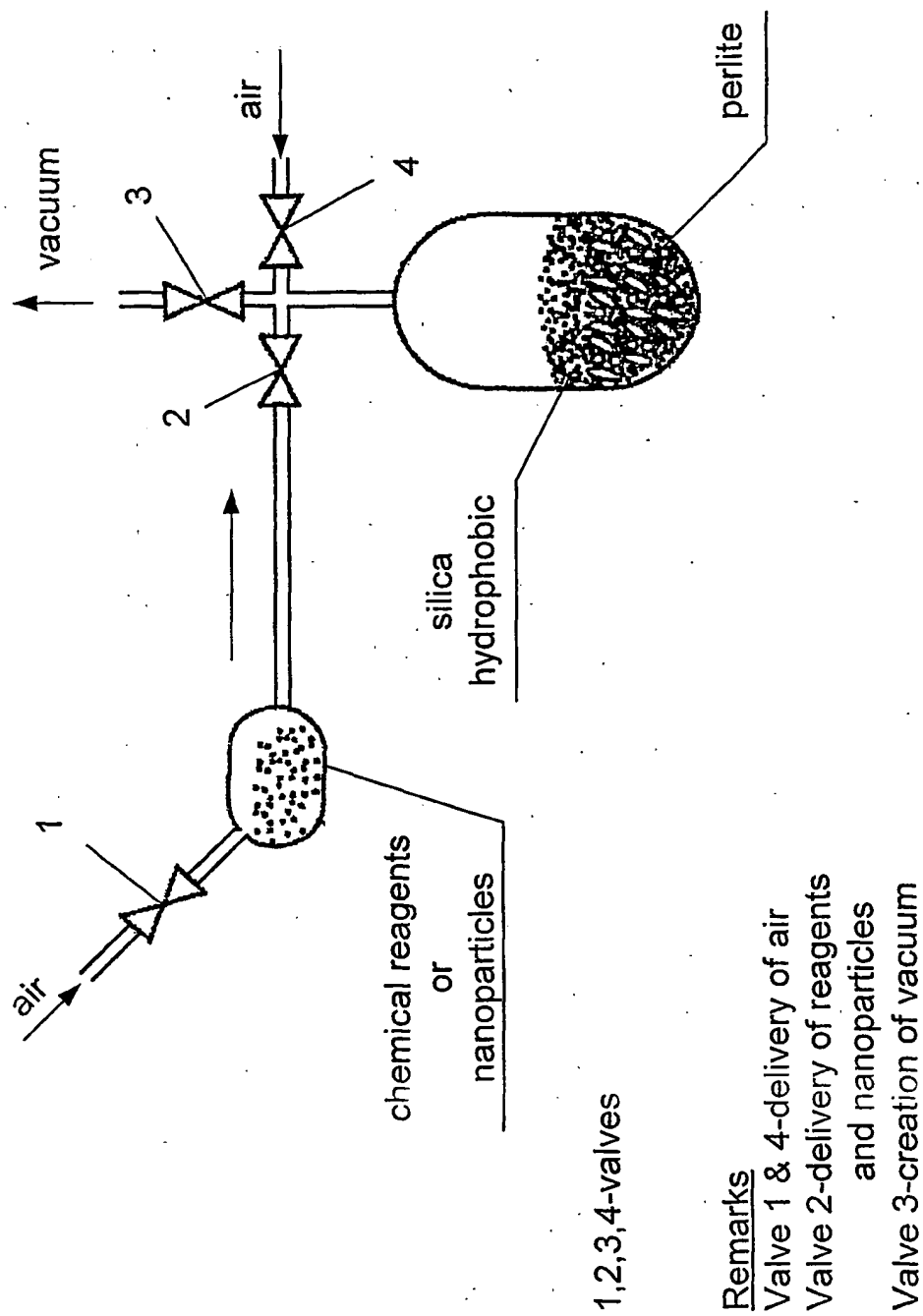
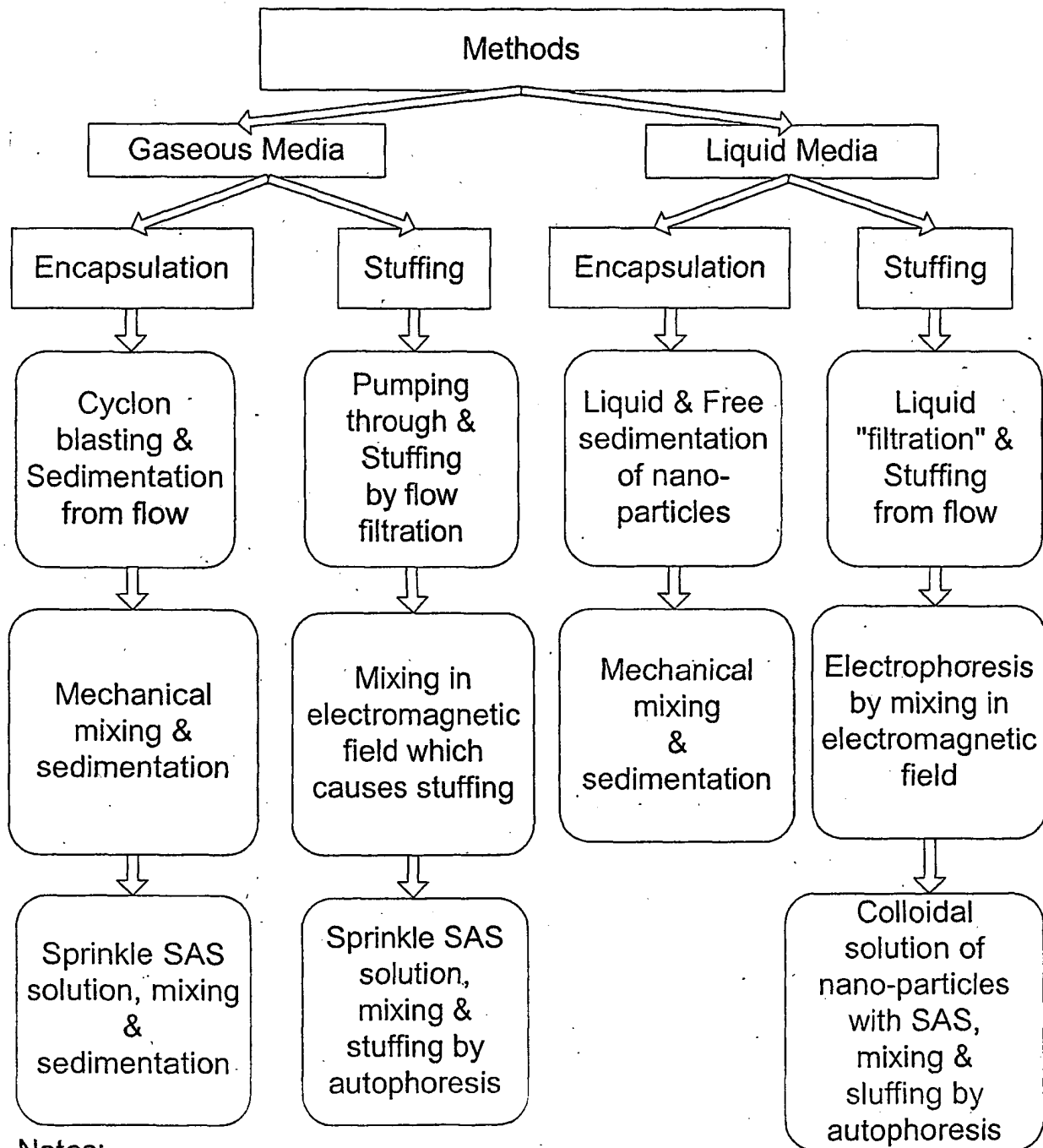


Fig. 3d. Scheme of encapsulation and/or stuffing  
of macro-particles with nano-particles

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Notes:

1. SAS is a surface active substance.
2. Gas may be pure inert carrier, air or other gas mix.
3. Liquid system may be based on water or organic solution, colloid, emulsion.

**Fig. 3e.** Summary of optional procedures for encapsulation and/or stuffing of macro-particles with nano-particles

## INTERNATIONAL SEARCH REPORT

Int'l Application No

PC 1/1 L 02/00305

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 B01J20/00 C02F1/28

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B01J C02F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

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| X          | DE 197 14 869 A (ETH UMWELTTECHNIK GMBH)<br>22 October 1998 (1998-10-22)<br>claims                                                   | 1-34                  |
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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\*Z\* document member of the same patent family

Date of the actual completion of the international search

16 July 2002

Date of mailing of the international search report

30/07/2002

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## INTERNATIONAL SEARCH REPORT

Int. Patent Application No.

PCT/IL 02/00305

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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Information on patent family members

In International Application No

PCT/IL 02/00305

| Patent document<br>cited in search report |   | Publication<br>date | Patent family<br>member(s) | Publication<br>date |
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